



## PATENT SPECIFICATION

NO DRAWINGS

1041593

Date of Application and filing Complete Specification: March 4, 1963.

No. 8588/63.

Application made In United States of America (No. 188,946) on April 6, 1962.

Complete Specification Published: Sept. 7, 1966.

© Crown Copyright 1966.

Index at acceptance:—A5 E(1A1B, 1A4A2, 1A4A3, 1A4A4, 1A4B2, 1A4B3, 1A5D, 1A7B, 1A11, 1A17)

Int. Cl.:—A 61 I 13/00

## COMPLETE SPECIFICATION

## Germicidal Toilet Bowl Cleaning Composition

We, THE DRACKETT COMPANY U.K. LIMITED, of 100 West Tenth Street, Wilmington, State of Delaware, United States of America, a company organised under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the art of toilet bowl cleaners and is directed more particularly to a toilet bowl cleaning composition having germicidal properties.

Through the years, a number of compositions have been proposed for use in cleaning toilet bowls or other receptacles having surfaces maintained for long periods of time in contact with water so as to subject them to staining by dissolved metallic salts, such as those of iron and copper, or encrustation with insoluble carbonate compounds, principally calcium carbonate and magnesium carbonate, precipitated from hard water. In order to dissolve these stains and encrustations, the cleaning composition must be strongly acidic and, for this reason, virtually all toilet bowl cleaners currently on the market utilize large amounts of sodium bisulfate. In addition, they often contain minor amounts of a compound capable of liberating carbon dioxide by reaction with sodium bisulfate, for example, sodium carbonate or sodium bicarbonate. The evolution of gas is advantageous for two reasons: first, it contributes a stirring action, bringing the surfaces to be cleaned uniformly in contact with the cleaning solution, and second, it aids in the dissolution of the solid cleaning agent. Small quantities of other materials may be also present, including various cleaning promoters, such as sodium chloride, one or more wetting agents as well as non-functional additives, such as perfumes.

From the intended use alone, one would immediately appreciate the value of providing

a composition of this type having germicidal properties. This goal, however, has proved difficult of attainment in practice. A great variety of chemical bactericides are known in the art but, almost without exception, their effectiveness is essentially destroyed at the very low pH's necessarily obtaining with the present class of compositions. For example, when a typical commercial bowl cleaner is diluted to the same extent as would be the case under ordinary conditions of use, the resultant solution has a pH in the order of 1.5—2. It is, of course, well known that numerous chlorine-containing compounds, both organic and inorganic, liberate chlorine under certain conditions, for instance, at an acid pH, and that chlorine itself in appropriate concentrations is a highly effective germicidal agent. However, the inherent instability of these compounds in a strongly acid environment, which is of advantage in causing release of the chlorine under the conditions of use, constitutes a serious disadvantage for the purposes of preparation and storage of the composition itself. Sodium bisulfate has definite hygroscopic tendencies and an initially dry mixture of this compound and a chlorine liberator attracts sufficient moisture to cause decomposition of the liberator. Moreover, in its usual commercial form, sodium bisulfate has a hydrated surface coating which is characterized by a relatively low melting point, say about 140°F. Thus, even assuming that moisture can be entirely excluded, if the mixture is subjected to a temperature of this magnitude, which is entirely likely in the course of transit in a box car or storage in a warehouse during the summer months, the surface coating undergoes melting and will react with the liberator. Consequently, as a matter of common practice, many manufacturers of unstable chlorine compounds specifically warn against admixing such compounds with strongly basic or acidic materials. Some purveyors of toilet bowl cleaners of the type in question have

[Price

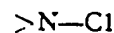
attempted to circumvent these difficulties by incorporating a strong bacteriostat. It is the nature of a bacteriostat to check or prevent bacterial growth so that the inclusion of such an agent gives the appearance of germicidal properties in that when a contaminated sample containing the agent is cultured, no growth will be observed due to the inhibiting effect of the agent. However, such agents are not capable of actually destroying bacteria unless large amounts are employed, which is impractical for reason of expense, and when their effect is discontinued, either by removal of the agent, as when the toilet is flushed, or by the addition of an antidote, the initially present bacteria flourish as freely as though they had never been exposed to the bacteriostat.

In United States Patent Specification 2,393,716 it was reported that stable solid mixtures of an acidic salt of an alkali metal and an unstable N-chlorosulfonamide could be obtained provided the aromatic radical of the sulfonamide was no more electro-negative than the phenyl radical. The principal example of satisfactory N-chlorosulfonamides was Chloramine B (sodium - phenyl - N - chlorosulfonamide). Actual experiments with this compound in association with the strongly acidic sodium bisulphate of the present composition, however, have revealed that a substantial loss in available chlorine, in the order of 25% of that initially present, is observed after contact for a period of approximately one week at temperatures of about 125°F. Consequently this specification does not constitute an answer to the problem of compounding a toilet bowl cleaner of the present type having germicidal properties.

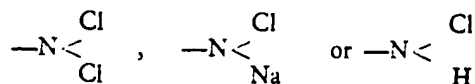
After much experimentation, all of which gave results of an unpromising nature, it was conceived that the reaction between the bisulfate and a chlorine-containing compound could perhaps be prevented by way of the addition of a solid, inert protective coating medium in finely divided form, such as a finely divided clay. When this concept was put into practice with inorganic chlorine-containing compounds, for example, calcium and lithium hypo-chlorite, which are probably the most widely used chlorinating agents at the present time, the results were no better than before. Thus, virtually all of the available chlorine was found to be lost after a few hours of exposure to elevated temperature irrespective of whether the protective coating medium was present or absent. After such discouraging performance with inorganic chlorine liberators and other conventional bactericides, it was altogether surprising and unpredictable to discover that a certain class of organic chlorine-containing compounds could be effectively protected against decomposition in the presence of solid sodium bisulfate by means of a minor amount of finely-divided inert pro-

TECTIVE COATING MEDIA TO THE EXTENT THAT LESS THAN 10% OF THE AVAILABLE CHLORINE THEORETICALLY PRESENT WAS LOST AFTER MANY HOURS OF EXPOSURE TO THE ELEVATED TEMPERATURE.

The organic chlorine liberators which release free chlorine when dissolved in water having an acid pH, which are found satisfactory for use in the present invention are, as a class, characterized by the presence of the following radical:



which may appear in the following forms:



For convenience, this class of compounds is referred to herein as the "organic chloramines". Extensive experimentation has failed to reveal any appreciable difference in the effectiveness for present purposes of a number of readily available compounds falling within this class, provided they are soluble in water. For example, the aryl and alkyl aryl chlorosulfonamides, preferably in the form of an alkali metal salt, have been found quite satisfactory. Examples of this group are chloramine-T (sodium tolyl-N-chlorosulfonamide), chloramine-B (sodium phenyl-N-chlorosulfonamide) and the chloro- and nitro-substituted derivatives of the phenyl group of the latter. Of equal suitability are the heterocyclic chloramines, of which may be mentioned potassium dichloroisocyanurate, trichloro-isocyanuric acid, 1,3-dichloro-5,5-dimethyl hydantoin, and N-chlorosuccinimide. The amount of available chlorine will, of course, vary from compound to compound and the quantity of chlorine actually released at the point of use will depend upon the quantity of the final composition that is employed. For these reasons, some adjustment in the proportion in the organic chloramine added to the composition may be desirable. As a general rule, it will be found that an amount of the organic chloramine in the range of 0.05—3.0% by weight of the total composition will release sufficient chlorine for good germicidal action when dissolved in water in reasonable quantities. Within this range, 0.1—1% is preferred. The form in which the organic chloramine is employed does not appear to be significant. It may, for example, be used as a finely divided powdered solid or as rather flat granules having a particle size of about 1/16th inch mean diameter. At levels of about 0.5% and higher, the odor of chlorine may be detected by the housewife and if this should be objectionable, a lesser quantity is recommended. The maximum of about 3% is the preferred upper limit. More

specifically, the organic chloramine should be included in sufficient quantity to provide at least 6 ppm of free chlorine at a reasonable use concentration of the composition and at least 18 ppm is even better.

5 Insofar as the cleaning constituents of the composition are concerned, they may be generally the same as is presently employed in the art. It is important that sufficient sodium bisulfate is provided to produce a pH of 5 or below at the reasonable use concentration referred to. As a practical matter, this will usually necessitate that the bisulphate predominate, i.e., constitute at least 50% by weight of the composition. Preferably, somewhat higher proportions of this ingredient are employed and 60 — 80% has been found quite effective. It is most convenient to employ sodium bisulfate in the form in which it is sold in large quantities by the manufacturers, namely as prills or small nodules having a particle size corresponding to 10—60 on the Tyler screen scale. Other forms could undoubtedly be substituted but are less easily handled and mixed in large quantities. All sodium bisulfate if exposed to the atmosphere for a sufficient period, acquires a surface coating in the form of the hydrate. This is immaterial for the purposes of the present invention, except to intensify the need for the protective medium.

As has already been indicated, it is better that the composition include a minor amount of compound which releases carbon dioxide by reaction with sodium bisulfate in the presence of water. While various compounds are suitable for this purpose, only sodium carbonate and sodium bicarbonate are ordinarily employed as a practical matter. Of these, sodium carbonate is perhaps preferred because of its relatively lower cost. As purchased by us, the sodium carbonate is in the form of particles having no regular size, but this particular form is of little or no consequence. The amount of the carbonate salt can vary within the range of 0.5 to 20% by weight, with about 5—15% by weight representing the preferred range. The bisulphate is, of course, consumed to a certain extent in the gas-producing reaction but when employed in the proportions indicated above a sufficient excess is available to tolerate this loss.

In addition to the carbonate compound, the composition of the present type often contains a chloride salt of an alkali metal, the most notable example of which is sodium chloride which can be present in the weight proportion of 0—20% but is preferably present in the same proportion as the carbonate compound.

60 For reasons that are not understood, such a salt tends to improve the cleaning effectiveness of the composition. At the low pH's obtaining at the reasonable use concentration, referred to, some of the salt may react to release HCl although this is difficult to prove experimen-

tally. Irrespective of the reason the presence of one of these salts has been found beneficial.

Several materials of rather diverse chemical nature have been found to be more or less equally useful as the inert protective medium of the present invention. For example, commercial clays, both calcined and uncalcined, of which at least 90% have a particle size of two microns or less have proved quite effective. In lieu of clay, one may substitute an inert heavy metal oxide, such as zinc oxide, or an alkali metal or heavy metal salt of a fatty acid, which salt is solid at temperatures up to 130—140°F, for example, sodium or zinc salts of oleic, stearic, palmitic, lauric and behenic acids. On the basis of our examination to date, the important characteristics of the protective medium appear to be inertness and a fairly high degree of sub-division. For example, compounds which would be expected to react with the bisulfate to form a surface coating of a relatively inert reaction product, e.g. magnesium carbonate, have not proved particularly effective. Insofar as the maximum permissible particle size is concerned, a precise upper limit is difficult to determine. It is believed that particles up to at least 100 microns would not seriously detract from the results obtained and this figure may not represent the extreme upper limit. In the case of clay, it is preferred that at least 90% have a size of 2 microns or less and the optimum of size of the heavy metal oxides or the soap may well be of the same order. The amount of the finely divided inert protective medium may range broadly between 0.5—20% by weight but only 1—5% is ordinarily required for good results.

Among the optional ingredients for the class of compositions in question may be mentioned perfumes, wetting agents and dyes. Usually, less than 1% by weight of each of these types of additives is all that is necessary. In order to give a visual indication of the initiation of germicidal activity, it is particularly valuable to utilize a dye which in the presence of free chlorine undergoes a distinct change in color. This change may be either from a colored to an uncolored state or from one color to another. Free chlorine is a strong oxidizing agent and has been found effective to change the color of most common organic dyes. Specific examples of dyes which behave in the desired fashion are Indigotine S. Conc., C.I. No. 73,015, and Light Green L.S.A. Conc. CF, C.I. No 42095. The former has been found to change in color from blue to water-white and the latter from green to water-white within about 15 seconds after a composition according to the invention containing the same is dissolved in water to form a dilute aqueous solution.

In order to demonstrate the improvement that can be achieved in the compositions of the present invention by virtue of the inert

protective coating medium, a series of experiments were carried out employing representative organic chloramines. For the purpose of these experiments, a set of basic compositions were prepared from 75 gm. of sodium bisulfate containing 2% moisture by weight, 10 gms. of sodium chloride, 10 gms. of sodium carbonate, and 4 gms. of one of the following protective media: clay, zinc oxide, and zinc stearate, along with a control consisting of the same mixture exclusive of any protective medium. The basic compositions were compounded by mixing the protective medium and bisulfate together, then adding the remaining ingredients and mixing until substantially homogeneous. To 25 gm. samples of the various basic mixtures thus formulated were added 50 mgs. of the following organic chloramines: Potassium dichloroisocyanurate, Chloramine-T, 1,3-dichloro-5-5-dimethylhydantoin and N-chlorosuccinimide. Each of the samples were enclosed within a glass bottle provided with a hand-tightened screw - type closure and placed in an oven maintained at 100°F. and heated for twenty hours. At the end of twenty hours, the bottles were removed from the oven and the samples analyzed to determine the amount of the chloramine remaining. The results are indicated in Table I:

TABLE I

Organic Chloramine	Protective Medium	Amount Chloramine Remaining (mg.)
Potassium di-chloro-iso-cyanurate	None	2
do.	Clay	47
do.	Zinc Oxide	47
do.	Zinc Stearate	48
Chloramine-T	None	16
do.	Clay	47
do.	Zinc Oxide	46
do.	Zinc Stearate	47
Chlorinated hydantoin	None	3
do.	Clay	49
do.	Zinc Oxide	43
do.	Zinc Stearate	43
N-chloro-succinimide	None	4
do.	Clay	51
do.	Zinc Oxide	51
do.	Zinc Stearate	50

The apparent increase of the N-chlorosuccinimide in some of the tests above the maximum amount possible is explained by experimental error.

In order to demonstrate the inadequacy of inorganic chlorinating agents for purposes of the present invention, the procedure summarized above in connection with Table I was

repeated, using the same amount of lithium hypochlorite and calcium hypochlorite in lieu of the organic chloramine, except that clay was the only protective medium tested, the moisture content in the bisulphate was maintained below 1% to eliminate as much as possible water as a factor contributing to decomposition of the chlorine compound, the

oven temperature was maintained at 125°F., hours of exposure. The results are reported and the samples were removed after sixteen below in Table II:

TABLE II

Chlorine Compound	Protective Medium	Amount Chlorine Compound Remaining (mgs.)
Lithium hypochlorite	None	1
do.	Clay	1
Calcium hypochlorite	None	2
do.	Clay	4

5

10

It will be observed that the decomposition of these common inorganic chlorinating agents took place at substantially the same rate, irrespective of the presence or absence of the protective medium.

The value of the protective medium for purposes of the relatively stable compound, Chloramine-B, was demonstrated by incorporating 1 gm. (1000 mg.) of Chloramine-B

into 499 gm. samples each of the basic mixtures described in connection with Table I, except that the bisulfate contained only 1% moisture by weight, sealing the samples in bottles as before, and aging the bottles at 125°F. for one week. The results of an analysis of these samples are summarized in Table III:

15

20

TABLE III

Chlorine Compound	Protective Medium	Amount Chlorine Compound Remaining (mgs.)	% Loss
Chloramine B	None	750	25
do.	Clay	960	4
do.	Zinc Oxide	920	8
do.	Zinc Stearate	920	8

One of the important advantages of the present invention is the simplicity in the mixing operation by which the present compositions are prepared. Thus, a single mixing step is all that is required, it being unnecessary to practice a preliminary coating step with any of the ingredients. In the mixing operation, all of the bisulphate is added to any commercial dry mixer, for example, a ribbon mixer, which is then set in motion. Next, the finely divided protective medium is introduced and tumbled with the bisulfate for a few revolutions, after which the remaining ingredients may be added at random. It appears to be important to the attainment of a satisfactory barrier action between the chloramine and bisulfate that the protective medium be co-mingled with the bisulfate before any of the other ingredients are introduced.

Reference has already been made to stan-

dard test procedures for determining the germicidal activity of commercial products. There are two such tests: the so-called "Use Dilution" method, which is the approved procedure of the Department of Agriculture, and the so-called "Webber and Black Method" which is the standard applied by the Food and Drug Administration. These are described in detail in "Official Methods of Analyses of the Association of Official Agricultural Chemists" (9th Ed.), pages 65-66 and 70-72, respectively. In general, the use dilution method is intended to test the ability of a particular germicidal solution to kill heavy concentrations of a given bacteria, such as *S. aureus*, *S. typhosa*, or *S. choleraesuis*, that have been previously applied to metal rings and dried, within a contact time not in excess of ten minutes. According to this method, ten metal rings are immersed in a medium which has

45

50

55

60

been inoculated with a particular bacteria in a concentration in excess of 100 million organisms per cc. The rings are then withdrawn and allowed to dry. When dry, they are placed in ten dry sterile tubes and the desired solution of the germicide to be tested is added to the tubes. After a contact time or not more than ten minutes, the rings are removed from the tubes aseptically and placed in a sub-culture media tube containing an appropriate nutrient together with a neutralizer for the residual germicide, if any. The sub-culture media containing the ring is incubated for 36-48 hours, which is entirely adequate for the growth of any organisms remaining alive after the treatment. In order to give a statistical confidence level of 95%, which is required to pass the tests, 50 tubes out of 50 so processed must show negative results, i.e. must be free of bacterial growth.

The Webber and Black Method demands that the germicidal agent must kill 99.999% of the organisms present, which may be either *E. coli* or *S. aureus*, within a contact time not in excess of 30 seconds. According to this procedure, 1 cc. of a medium containing 10 billion organisms per cc. is introduced with swirling by a pipette into 99 cc. of the germicidal solution to be tested. After the predetermined period of contact, i.e. 30 seconds or less, 1 cc. of the resultant solution is removed and added to 10 cc. of a sub-culture media containing a neutralizer for the residual germicide. The media is then incubated for 36-48 hours in petri dishes, so that any viable organisms will multiply, and at the end of this time, the bacteria population is counted. The number of organisms so counted must not exceed 0.001% of the initial bacterial population to pass the test.

Solutions of compositions according to the present invention are prepared for use in the above tests by dissolving 153 gms., i.e. 1/2 cup, of the composition in 2840 cc. of water, this being the recommended concentration for use in the home.

A preferred composition of the present invention is described in the following examples:—

50	Example	% by weight
	Sodium bisulfate	75
	Clay (sold under the trade name "Icecap K")	4
	Sodium carbonate	10
55	Sodium chloride	10
	Dye (Light Green SFA Conc.CF)	0.003
	Chloramine-B	0.4

The remainder of the composition to make up 100% may be composed of minute amounts of each of a perfume and a wetting agent (Ultrawet SKB). This formulation has been tested at the above indicated dilution accord-

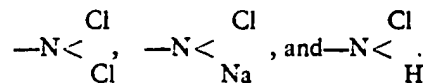
ing to both of the methods described above. Only about two minutes of contact time was required to pass the use dilution test and a 100% kill of the test bacteria after only 15 seconds of contact time was obtained in the Webber and Black test. Other compositions prepared within the ranges described herein will likewise give satisfactory results with these test procedures so long as the amount of the organic chloramine is so selected as to provide about 6 ppm of free chlorine in the use dilution test and about 18 ppm of free chlorine for the Webber and Black tests, each at the concentration level prescribed above.

In the above preferred embodiment, the other organic chloramines specifically enumerated herein may be substituted for the chloramines-B without lessening the performance of the composition to an unacceptable extent.

#### WHAT WE CLAIM IS:—

1. A solid particulate toilet bowl cleaning composition having germicidal properties, said composition containing as essential ingredients in admixture a major amount of sodium bisulfate and an organic compound containing at least one radical of the formula  $>N-Cl$  and which thus releases free chlorine when dissolved in water having an acid pH, and a minor amount of an inert protective coating medium in finely-divided form, serving to protect said organic compound from attack by said bisulfate.

2. The composition of claim 1 wherein said radical is selected from—



3. A solid particulate toilet bowl cleaning composition having germicidal properties comprising a substantially homogeneous admixture consisting of, by weight, at least 50% of sodium bisulfate, 0-20% of sodium carbonate, 0-20% of sodium chloride, and 0.05-3% of an organic chloramine as herein defined, with 0.5-20% of an inert protective coating medium in finely divided form, the coating medium serving to protect the organic chloramine from attack by the bisulfate.

4. A composition as in claim 3 wherein said medium is selected from the group consisting of a clay, a heavy metal oxide, and a metallic salt of a fatty acid.

5. A composition as in claim 3 wherein said protective coating medium has an average particle not greater than 100 microns.

6. A solid particulate toilet bowl cleaning composition having germicidal properties comprising a substantially homogeneous admixture consisting of, by weight, 60-80% of sodium bisulphate, 5-15% of a carbonate salt releasing carbon dioxide upon reaction with said bisulfate in aqueous

- 5 solution, and 0.1 — 1% of an organic chloramine as herein defined, with 1—5% of an inert protective coating medium in finely-divided form serving to protect said organic chloramine from attack by said bisulfate.
- 10 7. A composition as claimed in any one of the preceding claims wherein the bisulfate particles are coated with a coating of said finely divided protective coating medium serving to isolate said bisulfate from the chlorine releasing agent, said bisulfate particles being of relatively large size in relation to the particle size of said coating medium.
- 15 8. The composition as claimed in claim 7 wherein said bisulfate particles are granules of a size in the range of 10—60 mesh, Tyler scale, and said finely divided medium is of a particle size up to 100 microns.
- 20 9. A composition as claimed in any one of claims 3, 4 or 5 wherein at least 0.5% by weight of each of said carbonate salt and said sodium chloride is present.
- 25 10. A process of preparing a germicidal solid particulate toilet bowl cleaning composition having improved resistance to loss of germicidal activity during storage, which comprises the steps of agitating together a mixture of particles of sodium bisulfate and an inert, protective coating medium in finely divided form, said bisulfate particles being of a size such that a coating of said coating medium is formed on said bisulfate particles, the amount of said particles being at least 50% and said coating medium being 0.5—20%, and thereafter admixing with such mixture 0.05—3% of a solid, pulverulent, water-soluble organic chloramine as herein defined and any other ingredients, the percentages being by weight of the ultimate composition, and the said inert protective coating medium serving to protect said organic chloramine from attack by said bisulphate.
- 30 11. A toilet bowl cleaning composition when prepared by the process claimed in claim 10.
- 35 12. A solid particulate toilet bowl cleaning composition substantially as described in the example herein.
- 40 45

SEFTON-JONES, O'DELL & STEPHENS,  
Chartered Patent Agents,  
Beacon House,  
113 Kingsway,  
London, W.C.2.  
Agents for the Applicants.